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The Corrosion of Brass and Copper Fittings in  
Steam Heating Equipment



THE CORROSION OF BRASS AND COPPER FITTINGS  
IN STEAM HEATING EQUIPMENT

BY

WILLIAM THOREAU BRYANT

B. S. Texas Agricultural and Mechanical College, 1911

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

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IN

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

WILLIAM THOREAU BRYANT

ENTITLED THE CORROSION OF BRASS AND COPPER FITTINGS IN STEAM  
HEATING EQUIPMENT.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

*D. W. Parr*

Instructor in Charge

APPROVED:

*W. A. Noyes*

HEAD OF DEPARTMENT OF CHEMISTRY

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## INTRODUCTION.

The extensive use to which copper and brass fittings are employed in the various steam and hot water lines at the University of Illinois, and the rapid deterioration which occurs at times renders the subject of corrosion an especially important one. Each year a large number of copper and brass fittings has to be replaced with new ones, and it is needless to mention the numerous repairs, expense and annoyance caused by corrosive action. During the past few years considerable trouble has been experienced due to the decomposition of copper discs in steam traps that regulate the steam outlet from the radiators that are in service in the various University buildings. Examination of these discs shows corrosion in various stages often to the extent of pits or holes that extend through the metal.

The object of this investigation, therefore, is to determine the conditions which are responsible for the corrosion in the heating system at the University of Illinois with a view to prevention of the difficulty.

## HISTORICAL.

In the early days little trouble was met with from corrosion in the use of copper. It was frequently stated that trouble has only arisen in the last few years, but this is not altogether correct for we find that in 1823 Robert Mushet took out a patent for the manufacture of a corrosion resisting alloy suitable for sheathing which consisted of copper containing one eighth percent of tin or zinc, while in the following year Sir Humphry Davy



carried out a series of experiments on the best means of protecting the copper sheathing of ships from corrosive action of sea water. The records of the American Society of Naval Engineers show that serious and frequent trouble has been met with in the case of copper sheathings on vessels, while since 1900 the trouble has broken out with a still greater degree of destruction.

The Institute of Metals, being especially interested in the corrosion of metals, and realizing that an investigation into the nature and causes of corrosion was a big undertaking, appointed a Corrosion Committee for the purpose of collecting records of researches of the past workers and to carry on research work themselves on both the ferrous and non-ferrous metals. The work of this committee furnishes us with the most recent and thorough investigations on corrosion available at the present time.

The first thing that strikes one when reviewing this work is the very wide extent of the field to be explored. The work will probably take many years to complete, although practical results may be looked for much sooner. The Corrosion Committee (1) has already presented three reports on the subject of corrosion of non-ferrous metals. The first is a preliminary report dealing with the present state of knowledge in regard to the matter and throwing out some suggestions for research into the causes of corrosion of copper condenser tubes in sea water. Mr. G. W. Bengough is the author of the preliminary report and he has compiled an interesting summary of the chief researches published on the corrosion of brass, the theories that have been advanced to account for corrosion and the methods for prevention.





In the second report the Corrosion Committee describes experiments upon the corrosion of copper condenser tubes in sea water under varied conditions, whereas in the third report the results of an extensive study of the corrosion of brass is given.

A very brief summary of part of the second and third reports is thought essential here as many analogies can be made between the results given in these reports and the experimental work undertaken on the corrosion of copper and brass steam fittings.

The brass chosen by the Committee for special study was 70% copper and 30% zinc, the alloy being very commonly used in the various industries. This alloy has generally been considered to be a stable, homogenous, solid solution, though some considerable doubt has been thrown upon this view by recent work. Probably it is not a chemical stable body even at ordinary temperatures and at higher temperatures at which it is used.

The authors (2) divide the corrosion of brass into three types:

(a) Brass may lose both constituents at the same ratio, and both copper and zinc are then found in the corrosion product and in the proportions in which they are present in the original alloy. This is called "complete corrosion."

(b) It may lose one constituent only, - either copper or zinc. The corrosion product will then contain copper or zinc, - not both. This is called "selective" corrosion.

(c) It may lose both constituents simultaneously, but at different rates the corrosion product will then contain both copper and zinc but in a ratio which is different from that in which they



occur in the alloy. In addition to the three types given of uniform corrosion, local action may occur at various points on the metal's surface. This localized action may be "complete" or "selective" corrosion. The first produces pits and in the second a spongy copper or an alloy richer in zinc is formed. Very frequently in practice these products of a selective local attack are worn away mechanically, and the final result is, as in the case of "complete" localized corrosion, the formation of a pit.

Some of the many factors which determine the character of corrosion is necessarily to be considered here and the following are a few that are considered the most important, and taken from the report of the Corrosion Committee are placed in their respective order of importance as nearly as possible:

- (a) The composition of the alloy
- (b) The temperature
- (c) Aeration of the water.
- (d) Concentration of the mineral content of the water.
- (e) The catalytic action of the oxy-salt of zinc and copper
- (f) The physical condition of the metal.
- (g) Contact with electro negative substances, such as carbon

(a) The composition of the metal: The rate of corrosion of copper in sea water at ordinary temperatures is diminished by alloying it with zinc. This diminution increases rapidly as the proportions of zinc is increased until it reaches a minimum when the alloy contains an equal number of atoms of copper and zinc. An alloy 50% copper and 50% zinc appears to be almost unattacked by sea water at ordinary temperatures.





(b) The initial rate of corrosion of 70/30 brass in sea water increases as the temperature rises from 15° to 50° C but between 50° and 60° C the rate appears to fall off very quickly, for at 60° it is less than at 30° C.

The rate of corrosion falls off with time, and more rapidly at higher temperatures than at low, although the initial rate of corrosion after a given time will be smaller. It is interesting to note in connection with the rates of corrosion that pure copper dissolves readily in sea water at first, but the rate of solution gradually diminishes owing to a formation of a protective film, possibly an oxide.

(c) At ordinary temperatures the aeration of sea water increases the initial rate of corrosion. At 50° C. it is very slight while at 60° it diminishes the rate of corrosion. At 15° C the rate of corrosion is greater in aerated sea water than at 50° C. Thus the effect of aeration appears to be greatest at low temperatures. The corrosion of pure copper in sea water is checked by aeration after a time owing to a formation of an oxide film, while the corrosion of zinc is considerably accelerated.

(d) Dilution of sea water: Diluted sea water attacks 70/30 brass more slowly than ordinary sea water. Aerated sea water that has been diluted twice its volume with distilled water dissolves the copper or the brass faster than the zinc whereas when the sea water has been diluted 16 times zinc will dissolve the faster. The solubility of  $O_2$  and  $CO_2$  is greater in dilute sea water than in ordinary water. It is possible, therefore, that the increase of  $O_2$  and  $CO_2$  content in the more dilute sea water and the decrease in



in salt content is an explanation of this action.

It has been found that distilled water contained in an open beaker and kept saturated with  $\text{CO}_2$  will dissolve zinc from 70/30 brass. This action is small at high temperatures. It was shown that sea water aerated by air which is free from  $\text{CO}_2$  has very little action upon zinc. Therefore  $\text{CO}_2$  plays an important part in the solution of zinc of the brass. To what extent the influence of dissolved  $\text{O}_2$  and  $\text{CO}_2$  upon the course of corrosion was not satisfactorily obtained.

The solubility of pure copper in gently aerated sea water is diminished by the dilution of the sea water and is greatest in distilled water. It appears from this that the dissolved salts are responsible for the solution of copper and the water, and the gases for the solution of the zinc.

#### THEORETICAL

In order to have as good an idea as possible concerning the complicated problems of corrosion it is necessary to consider some of the theories as to the cause of corrosion of copper and brass factors that govern this decomposition, and as far as possible, modes of prevention.

Copper and brass fittings are prepared for special industrial uses where they find valuable applications on account of certain properties which they possess, either withstanding corrosion altogether or corroding in such a manner which does not materially affect the use of the metal.





In a general way it may be stated that there are four types of corrosion usually met with:-

(a) Corrosion from ordinary atmospheric effects.

(b) Corrosion from special atmospheric conditions; for example, in the manufacturing centers where air is less pure.

(c) Corrosion in special media such as gases, acids, or other liquids.

(d) Corrosion by heating effects. This is usually termed oxidation, but it is, of course, more or less corrosion.

On the other hand to cope with these conditions we find two general classifications of materials that are commonly used:

(1) The pure metal.

(2) Metals which are alloyed to increase the non-corrosive properties. In the first case we find copper, and in the second case we find a large number of alloys which are designed to resist corrosion to meet the varied needs in the commercial field.

The corrosion of copper and its alloys has yearly been forced upon the notice of engineers by many instances of failure of these metals when subject to conditions under which previously they had been found to be sufficiently resistant. These metals are employed because their durability is greater than the cheaper and stronger metal iron.

Bearing in mind the nature of the uses to which they are put, the importance of the conditions influencing corrosion need mentioning. Many of the instances of failure recorded show that causes tending to promote corrosion are of complicated character. It is often found that corrosion occurs in one case and not in





another where parallel conditions exist. Again in many cases when corrosion occurs the deterioration of the metal does not at once reveal itself, and in other cases is only apparent when rupture takes place. It is very unfortunate that these conditions cannot be entirely determined in the laboratory and corrected for, thus saving annoyance and expense. Laboratory tests on corrosion are commonly made for the purpose of determining which of the several materials will offer the greatest resistance to corrosion when exposed under certain specified conditions. It is impossible to reproduce these conditions exactly on account of the long duration of the tests. In order to hasten the tests active chemical corroding agents are commonly adopted. Such tests are usually of an unsatisfactory character. A number of metals or alloys arranged in order of their resistance to acids and alkalies will often present a very different order when exposed to technical conditions.

The rate of corrosion of any metal will depend on the solubility of the product and on the renewal of the solvent to prevent saturation taking place. In some cases the first product of the action may be soluble but the removal in the solution may be prevented by secondary reactions resulting in the precipitation of some of the dissolved matter. This is as near to any general statement that can be given relative to corrosive action of a metal. Realizing that the rate of corrosion depends entirely on conditions encountered, and that these factors are numerous and varied, it was decided to study the corrosion of copper and brass steam fittings in use at the University of Illinois, and the results obtained together with any bearing they may have on the subject of corrosion



of copper and brass will be given in this paper.

A study of the radiators that are in service in the various buildings was decided the essential starting place for experimental work as more trouble has occurred here due to the rapid corrosion of the copper and brass fittings on the pipes that lead to and from the radiators.

On examining the radiators it was found that gases often accumulated to such an extent as to form dead ends, thus preventing the passage of steam and water through the system which afforded an excellent opportunity for obtaining gases for analysis that evidently pass through the system along with the steam and water. Accordingly a study of these gases suggest itself as a logical starting place to begin the experimental work.

#### EXPERIMENTAL WORK.

The samples of gas for analysis were taken from the different buildings where the gas had accumulated in the radiators to such an extent as to cause stoppage of the circulation of steam. A 500 cc. glass sampling tube of the ordinary oblong type was filled with a saturated brine solution in order to prevent any of the gas from being absorbed, and connected to the gas outlet of the radiator by a rubber tube filled with water to prevent air from being drawn into the flask. The gas samples were immediately brought to the laboratory and analysis made. In no case was an analysis made of gas that had remained in the sampling tube longer than six hours. This was considered necessary as often the very best sampling tubes would show leaks after standing for a long period of time.





A water jacked burette using mercury as the confining liquid and accurate to .1% was used for measuring the gases. The apparatus consisted of a graduated tube of 100 cc. capacity graduated to read in tenths of a centimeter. The measuring tube and correction tube stood in a wide glass cylinder filled with water to insure uniform temperature. The apparatus was calibrated and all connections were made with heavy black gum rubber tubing and firmly wired to prevent any leaks.

The carbon dioxide was first absorbed by passing the gas into a 50% solution of potassium hydroxide. Oxygen was absorbed by alkaline pyrogallol solution, and carbon monoxide was removed by ammonical cupric chloride solution. In determining the combustible gases two methods were tried:

(1) Combustion in an explosion pipette as commonly used for technical gas analysis (3)

(2) Combustion in a platinum capillary tube, Drehschmidt type improved by Winkler (4). No hydrogen or methane could be detected by either of the methods, and to make sure that such gases did not occur in too small quantities for combustion hydrogen was introduced and the mixture exploded and was analyzed. The results in every case showed that neither hydrogen nor methane existed.



Analyses of Radiator Gases Taken from Various  
Places in the Chemistry Building.

Place	Date	% CO <sub>2</sub>	% O <sub>2</sub>	% CO	% H <sub>2</sub>	% N <sub>2</sub>	% NH <sub>3</sub>
3rd floor	Feb.20	12.58	17.22	--	--	69.20	Trace
3rd floor	Feb.21	13.32	17.42	--	--	69.26	Trace
1st floor	Feb.22	0.20	20.70	--	--	79.10	Trace
3rd floor	Mar.11	36.40	12.08	--	--	51.52	Trace
1st floor	Feb.22	00.20	20.85	--	--	78.95	Trace
3rd floor	Mar. 3	36.60	12.28	--	--	51.12	Trace
3rd floor	Mar. 2	57.00	8.52	--	--	34.48	Trace
3rd floor	Mar. 3	56.00	7.45	--	--	36.55	Trace
1st floor	Mar 6	19.16	14.91	--	--	65.93	Trace

Engineering Bldg.\*

1st floor	Feb.25	--	21.00	--	--	79.09	--
1st floor	Feb.25	0.03	20.58	--	--	79.09	--
3rd floor	Feb.27	0.02	20.80	--	--	79.18	--
3rd floor	Feb.28	0.01	20.54	--	--	79.45	--
3rd floor	Feb.21	0.08	20.08	--	--	79.84	--

\* A strong vacuum was maintained in this building and few cases of gas bound radiators were found. The analysis indicates air had been drawn into the system through leaks.





## University Hall\*

Place	Date	% CO <sub>2</sub>	% O <sub>2</sub>	% CO	% H <sub>2</sub>	% N <sub>2</sub>	% NH <sub>3</sub>
2nd floor	Mar. 2	10.90	17.25	--	--	71.85	--
4th floor	Mar. 5	7.00	16.94	--	--	76.94	--

\*A large number of gas bound radiators were found in this building but only a few samples could be obtained on account of the construction of the radiators, most of them being very old types with no provision for gas outlet. No gas accumulation in radiators were found on the first floor, while on the third and fourth many were found containing gas.

Agricultural Building\*\*

2nd floor	Mar. 2	1.68	20.15	--	--	76.17	--
Morrow Hall	Mar. 2	--	20.80	--	--	79.20	--
1st floor	Mar. 3	2.73	19.85	--	--	77.42	--

\*\* The construction of the radiators prevented the obtaining of many samples that were desired. A large number of gas bound radiators were found in this building.

Woman's Building.

1st floor	Apr. 1	38.40	10.86	--	--	49.26	Trace
3rd floor	Apr. 1	48.47	9.31	--	--	42.22	Trace
2nd floor	Apr. 2	49.23	9.06	--	--	41.71	Trace
1st floor	Apr. 2	19.02	14.90	--	--	66.08	Trace
2nd floor	Apr. 3	66.57	4.85	--	--	28.58	Trace
2nd floor	Mar. 6	7.14	19.28	--	--	73.58	--

All of the radiators in this building were found to be either totally or partly gas bound. Corrosion was found to be greater here than in any of the buildings.



### Discussion.

The analysis of all the gases examined corresponds closely to the old generally accepted idea that these gases are atmospheric oxygen, nitrogen, and perhaps carbon dioxide. Nevertheless, it is very interesting to note the high percentage of carbon dioxide and the decrease in oxygen content when compared with air. The apparent inconvenience that results from these gases is a stoppage of the circulation of the steam and the bearing they have on corrosion which will be given in this paper. A brief description of the system will give a better understanding of the accumulation of these gases in the different locations examined.

On examining the radiators in the various buildings, it soon became evident that in some buildings a large number of radiators were gas bound, while in others none could be found. Dead ends were found in all the systems but the vacuum systems were fewer in number in comparison with the one and two-pipe gravity system. Why should some buildings be favored with less stoppage than others? It was found that the buildings that were free from dead ends were near the vacuum pumps located on the main return lines. This reason first suggested itself but was misleading for awhile on account of some exceptional cases which was afterwards found to be caused by either the pump not working properly or else they were too small to handle the return water from the building. A pump is located at the Natural History Building which pulls the return water from this building, the Chemistry and the Agricultural Building. Not a single case of gas bound radiators were found in the Agricultural Building. I think this also explains why the first floors are nearly always free from gas while accumulations are found on the upper stories.





Much trouble was encountered the past winter in the Woman's Building, Lincoln Hall and the Commerce Building with the stoppage of circulation due both to gases and settlement accumulating. The pump on the return line is small and does not handle the water properly; also in the case of Lincoln Hall the return pipes from the radiators are very small and easily choked with sediment. Similar difficulties in the various buildings could be enumerated where different factors enter that cause improper working conditions.

#### Accumulation of Gases in Radiators.

Take, for example, a steam heating system made up of a boiler with steam pipes leading to various mains and radiators from which return pipes bring the condensed steam back to the boiler and enters below the water line. The plant is run with no addition of water after the boiler has been originally charged; no steam is blown out. The closed system usually contains, when in actual running condition, a number of dead ends where gases have accumulated and the pipes are cold. This may be observed in the radiators of common type, both in the hot water and steam systems. In this cooler part of the system, such gases as oxygen ( $O_2$ ), and carbonic acid ( $H_2CO_3$ ) which originally were in the feed water or had been sucked in from the air will collect. Here they will dissolve in the condensed water which is to be returned to the boiler, carbon dioxide and ammonia being especially soluble. The carbonic acid or its active hydrogen will cause the solution of iron as well as copper as will be shown.

#### Possible sources of Oxygen ( $O_2$ )

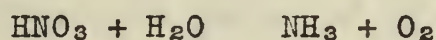
From the gas analyses made (5) indications point to leaks



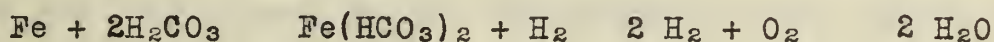


in the system, especially so where vacuum systems are in use. The same may be true in the gravity system. The vacuum produced by the condensed water that fills the pipes is forced onward by back pressure.

Nitrates may be a source of oxygen but not probably under the conditions found. After all the dissolved oxygen has been used up nitrates are completely reduced to ammonia and oxygen.



The various gas analyses varied in oxygen from 8.50% to 20.60%, larger percent clearly indicating air while the decrease in oxygen may be accounted for by the following reaction:



The action of the free carbonic acid produces hydrogen and the large amount of oxygen in the radiator gases and the oxygen dissolved in the water would oxidize hydrogen back to water. If the above reactions take place one would naturally expect to find a large amount of iron oxides in the water over which the gas ran low in oxygen. This was the case but such varied amounts of iron was found in the waters examined that no conclusive evidence could be obtained.

#### Source of Carbonic Acid.

The large amounts of carbonic acid found in the radiator gases can be easily accounted for on examining the analysis of the water supply. The amount of carbon dioxide is approximately 2% per 1000 gallons of water, - a source of 400# per day based on an average winter's day supply. The water becomes saturated with the gas and the excess which is large on account of the high temperature



is discharged by the heat along with the steam.

These gases accumulate in the higher levels in the circulation systems and under certain conditions may fill the pipes to the exclusion of the steam and thus prevent an outlet for the condensed water. This water becomes thoroughly saturated with the varied gases and salts, causing harmful effects on the copper and brass fillings.

#### Source and Amount of $\text{NH}_3$ in Gases

Only minute traces of ammonia gas was found on analyzing the gas. The reason for this can be explained if we bear in mind that the samples of gases taken were from radiators where stoppage of circulation had been caused by the accumulation of the gases, the condensed steam being cold in every case absorbed the ammonia gas. Examinations of the various waters taken from the radiators where dead-ends were found confirms the above explanation.

In many cases qualitative examination of the steam was made which gave conclusive evidence that ammonia was being carried through the systems in this way. More will be said about ammonia under the discussion of corrosion due to ammonia in the water.

Tests were carried out by suspending copper and brass strips in Erlenmeyer flasks filled with gas. The strips were carefully weighed on a five place assay balance and then placed in the Erlenmeyer flasks and allowed to stand two and three weeks in the presence of the gas. All corrosive tests made with gases out of contact with water gave negative results. On the other hand, when these gases are absorbed in water a very corrosive action was obtained. Further reference will be made of this under corrosive action of radiator water.



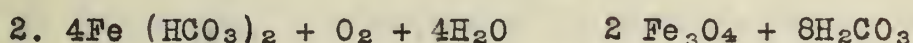
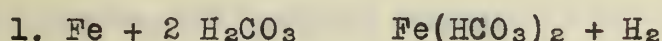




### Chemical Action of Carbonic Acid.

The report of the New York City Committee on Water Supplies (6), Dr. Friend (7) and many other noted investigators have shown that the action of carbonic acid is a catalytic one (8) as long as there is any dissolved oxygen in the water.

In case of iron the following reactions have been found to take place:



According to reactions #2 only one part of oxygen to four parts of water enter in, and equation #3  $\text{Fe}_2\text{O}_3$  acts as an oxidizer and water unites with the reaction setting free carbonic acid. These reactions clearly show how a very small amount of dissolved oxygen can carry on the formation of carbonic acid almost indefinitely and a large amount of iron corroded relative to the amount of dissolved oxygen. For example, ten parts per million of dissolved oxygen produces 126 parts per million  $\text{Fe}_3\text{O}_4$  expressed as iron (Fe), Theoretical amount.

### Chemical Action of Oxygen.

Much experimental work can be found in the current literature on the corrosive effect of absorbed oxygen and carbonic acid in water on iron and steel, especially in service pipes where hot water is circulated. In many cases copper and brass piping has to be used on account of the intensive corrosive action due to these absorbed gases. (8)

The research laboratory of the National Tube Company reports



that "free oxygen and carbonic acid in water have been proven to be the cause of practically all the trouble with hot water supply lines, as these gases are retained in the water with the closed system of heating and is used almost universally in this country. Two methods are proposed for removing these gases from water:

1. By reducing the pressure of the heated water. For example, by the use of an efficient "open" type heater under atmospheric pressure or partial vacuum.
2. By keeping the hot water in contact with a large surface of iron under pressure for a sufficient length of time to remove and "Fix" the oxygen and carbon dioxide.

The latter principle has been in use at two plants during the past year at the Research Laboratory and Hospital Building of the National Tube Company and Irene Kaufmann Settlement, Pittsburgh, Pennsylvania. Also several hot water heating systems as used in residences, were installed for experimental purposes and conclusive evidence according to the Research Department has been obtained to show when oxygen and carbon dioxide has been removed. The corrosion of iron and steel pipes can be arrested and practically eliminated. (9). The average oxygen content of the water used at the Irene Kaufmann Settlement was 8 cc. per liter and after treatment 0.5 cc per liter. This amount of oxygen, 8 cc per liter, has such a corrosive effect to require new pipes every year. Once rust starts the action is accelerated, so that the arresting of corrosion of old pipes is of great significance.

Along with the tests made by the National Tube Company with hot water system radiators, the Pittsburgh Testing Laboratory







carried out corrosion tests under the same conditions. Dr. J. O. Handy, Director of the laboratories, in his report says that the treated water for the removal of oxygen gave 62 to 85 percent less corrosion, based on the deepest pitting in the pipes carrying untreated water.

After treatment the water still carried considerable gas in solution which on analysis shows an average of 20% hydrogen and the rest nitrogen. The oxygen in the untreated water frequently ran as high as 26 to 30% of the volume of dissolved gas ( 10). It is interesting to note that the conclusions drawn from these experiments seem to conflict with the views of Dr. Whitney that it is the active hydrogen that causes the corrosion. Both theories can be satisfactorily explained by the electrolytic theory and in reality both are right as far as the subject of corrosion is known.

Experiments on the corrosion of copper by small amounts of ammonia dissolved in the water shows that the rate of corrosion depends entirely on the other material contained in the water. It was shown that water containing 100 P.P.M. of ammonia in pure water had more than twice the corrosive action that the same amount in water containing bicarbonates and oxygen dissolved in it, in view of the fact that sodium bicarbonate in pure water has an intensive corrosive action on copper. This was found true at temperatures from 20° C. to 95° C. A protective coating seems to form that prevents further corrosion of the copper. There is a possibility that similar actions under certain conditions could happen in the case of iron and steel.



## PART. II.

## The Examination of the University Radiator Water.

## Introduction.

A study of the radiator water was made in an attempt to find out what corrosive effect the relative amounts of ammonia, absorbed oxygen and carbon dioxide might have on copper and brass fittings as used in the University heating systems.

The samples of water for analysis were taken from the various radiators where steam circulation had been stopped and condensed water had accumulated to such an extent as to fill the radiators and return steam pipes that furnish an outlet for the condensed water and steam to the main line. On this return pipe about six inches from the base of the radiator is located a valve that governs the passage of the returning steam, and here it was found an ideal place to obtain samples of water for study, as the water that was standing around the copper discs of the valves could be obtained. The pipe connecting the valve to the radiator was disconnected; the valve then opened and about 500 cc. of water obtained which was placed in an Erlenmeyer flask and brought to the laboratory and examined for ammonia. It was found necessary to determine the ammonia by Nessleration, taking one centimeter of the water for each determination. One sample in each radiator examined was also tested for absorbed oxygen and carbon dioxide, the oxygen being determined by titrating with a fiftieth normal potassium permanganate solution, and the free carbon dioxide content determined by adding an excess of standard barium hydroxide and titrating with a tenth normal sulphuric acid solution.







It was thought well to tabulate these results according to the buildings where they were obtained as varied factors enter in each case.

Lincoln Hall

Feb. 18, 1917.

(I)

Floor	Reading	P.P.M. NH <sub>3</sub>
1st, Room 113 -----	0.60 -----	7.20
3rd -----	1.90 -----	24.00
3rd, Room 426 -----	0.20 -----	2.40
3rd, Room 418 -----	0.20 -----	2.40
4th, landing -----	0.20 -----	2.40
3rd, landing -----	20.00 -----	240.00

March 2, 1917.

1st, Room 114 -----	0.20 -----	2.40
1st, Hall -----	0.20 -----	2.40
1st, Hall -----	0.20 -----	2.40
1st, Hall -----	0.20 -----	2.40
2nd, Hall -----	0.20 -----	2.40
2nd, Hall -----	0.60 -----	7.20
2nd, Hall -----	1.00 -----	12.00
3rd, Hall -----	0.20 -----	2.40
3rd, landing -----	10.00 -----	20.00
3rd, Hall -----	0.20 -----	2.40

March 23, 1917.

3rd, Room 311 -----	0.20 -----	2.40
3rd, Hall -----	1.00 -----	12.00
3rd, West end hall -----	0.20 -----	2.40
3rd, Hall -----	0.70 -----	8.40



## (I) Continued.

Floor	Reading	P.P.M. NH <sub>3</sub>
3rd, Hall -----	0.20 -----	2.40
3rd, Hall -----	4.00 -----	48.00
3rd, landing -----	0.70 -----	84.00
Basement -----	0.20 -----	2.40
4th, Room 411 -----	0.20 -----	2.40

Agricultural Building

1st, Dairy Lab. -----	0.80 -----	9.60
1st, Hall (water hot) ----	6.00 -----	72.00
1st, Hall (water warm) ---	6.00 -----	72.00
1st, Hall (water warm) ---	0.20 -----	2.40
1st, Dairy Lab. -----	1.20 -----	14.40
1st, Hall -----	0.70 -----	84.00
2nd, Room 556 -----	0.10 -----	1.20
2nd, Hall -----	9.00 -----	108.00 (valve eaten out)
2nd, Morrow Hall -----	4.00 -----	42.00
2nd, Morrow Hall (warm water)	2.50 -----	30.00
3rd, Room 302 -----	8.00 -----	96.00

Physics Laboratory.

1st, Hall -----	3.00 -----	36.00
1st, Hall -----	0.20 -----	2.40
1st, Hall -----	1.90 -----	22.80
2nd, Hall -----	0.20 -----	2.40
2nd, Hall -----	0.80 -----	9.60
3rd, Hall -----	0.80 -----	9.60
4th, Hall -----	0.80 -----	9.60





Woman's Building.

Feb. 28, 1917.

Floor	Reading	P.P.M.	NH <sub>3</sub>
1st -----	0.20 -----	2.40	
2nd -----	0.80 -----	96.00	
2nd -----	0.60 -----	72.00	
3rd, -----	8.00 -----	216.00	
4th -----	0.20 -----	2.40	

March 23, 1917.

1st -----	1.00 -----	12.00
1st (old part) -----	1.80 -----	21.60
1st (reception room) ----	0.70 -----	8.40
1st (reception room) ----	0.20 -----	2.40
1st, Hall -----	0.60 -----	7.20
2nd, Hall -----	7.00 -----	84.00
3rd, Hall -----	45.00 -----	540.00
	(average of 10 determinations)	
3rd, West Hall -----	10.00 -----	120.00

Natural History Bldg\*.

Basement -----	0.20 -----	2.40
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\*Strong vacuum. All radiators were found working on three inspection trips. (only one in basement not)



Commerce Building.

February 18, 1917.

Floor	Reading	P.P.M. NH <sub>3</sub>
1st (warm water) -----	0.20 -----	2.40
1st, Hall -----	0.20 -----	2.40
2nd, landing -----	3.00 <sup>0</sup> -----	36.00
4th, Hall -----	9.00 -----	108.00
4th, Hall -----	12.00 -----	144.00
4th, Hall -----	0.40 -----	4.80

March 23, 1917.

1st, Hall (south end) --	1.20 -----	14.40
1st, lecture room -----	0.20 -----	2.40
1st, Hall -----	1.00 -----	12.00
2nd, Landing -----	3.00 -----	36.00
2nd, landing(south end)	0.20 -----	2.40
3rd, landing -----	1.80 -----	21.60
3rd, Hall -----	0.20 -----	2.40
3rd, Room 308 -----	1.80 -----	21.60

Auditorium.

Hall -----	0.20 -----	2.40
Hall -----	7.00 -----	84.00
Hall -----	3.00 -----	36.00
Hall -----	1.00 -----	12.00

Law Building.

2nd, Hall -----	2.00 -----	24.00
1st, Hall -----	0.30 -----	3.60
1st, Hall -----	0.20 -----	2.40
3rd, court room -----	2.00 -----	24.00





Armory.

Sample	Reading	P.P.M. NH <sub>3</sub>
I -----	0.20 -----	2.40
II -----	0.20 -----	2.40
III -----	0.20 -----	2.40
IV -----	0.20 -----	2.40
V -----	0.20 -----	2.40
VI -----	0.20 -----	2.40

Samples represent a complete circuit of the Armory. A strong vacuum was on and all radiators were working good when examined.

University Hall.

1st, Hall (water warm) --	0.20 -----	2.40
2nd, Room 211 -----	3.00 -----	36.00
4th, Room 401 -----	0.20 -----	2.40
5th, Room 521 -----	0.20 -----	2.40

Chemistry Bldg.

March 2, 1917.

1st, Room 125 -----	0.20 -----	2.40
1st, (old part) -----	0.20 -----	2.40
2nd, (Dr. Noyes rec. room)	0.30 -----	3.60
4th, (Qual. Lab. old part)	16.00 -----	192.00
4th, -----	2.50 -----	30.00

Strong vacuum in new part.

Transportation Bldg.

2nd, (strong vacuum) ----	0.20 -----	2.40
1st (strong vacuum) -----	0.20 -----	2.40

Very strong vacuum.



Hydraulic Laboratory.

Floor	Reading	M.M.P.	NH <sub>3</sub>
1st (water hot) -----	0.20 -----	2.40	
2nd (water hot) -----	0.20 -----	2.40	

Strong vacuum; all radiators working in good shape.

Engineering Building.

1st, Room 109 -----	4.00 -----	48.00	
1st, Hall -----	0.20 -----	2.40	
3rd, Hall -----	0.20 -----	2.40	
3rd, Hall -----	0.20 -----	2.40	

## Discussion.

The analysis of the water from the radiators shows an ammonia content varying from two parts per million to over five hundred parts of ammonia. This concentration of ammonia can be accounted for if we bear in mind that the gases that pass through the heating system seeks the higher levels in the circulation to such an extent as to cause the stoppage of the circulation of the steam. The steam condenses at these places and forms what is commonly termed "dead ends" and it is in such locations we find the water containing the varying amounts of dissolved ammonia, although 500 parts per million of ammonia was the greatest concentration found. We cannot conclude from this that higher concentrations may not occur. Two cases in this locality (11) have been mentioned where evidently the ammonia and carbon dioxide became concentrated enough to precipitate out causing a stoppage in the system. The first case occurred in a





steam heating system of a dwelling near the University. The riser which conveyed steam to a radiator on the upper floor was found to be stopped up. Upon cutting out a section of the pipe where the obstruction had occurred it was seen to be a white, crystalline solid completely filling the pipe and extending longitudinally for 5" to 6".

Ammonia -----	21.35%
Carbon dioxide -----	49.80%
Water & undetermined -----	<u>28.85%</u>
	100.00%

As will be seen this compound corresponds most nearly to ammonia bicarbonate. The quantity of raw water used in the boilers supplying the steam approximates 100,000 gallons daily, which would furnish enough carbon dioxide and ammonia for fifty pounds of the ammonium salt daily, provided it were all brought under suitable conditions for its formation. The ammonium bicarbonate decomposed at temperatures from 40 to 60 C., hence the combination of the separate gases to form the salt would take place at somewhat lower temperatures. The raw water used in the boilers to supply steam for the radiators is a very soft water. The analysis shows:

Material	P.P.M.	Grains per gallon
KNO <sub>3</sub> -----	2.30 -----	.130
KCl -----	.80 -----	.050
K <sub>2</sub> SO <sub>4</sub> -----	2.00 -----	.110
K <sub>3</sub> CO <sub>3</sub> -----	6.40 -----	.370
Na <sub>2</sub> CO <sub>3</sub> -----	81.70 -----	4.770
NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> -----	7.50 -----	.430
MgCO <sub>3</sub> -----	105.3 -----	6.140
CaCO <sub>3</sub> -----	144.8 -----	8.450
FeCO <sub>3</sub> -----	4.4 -----	.26
Al <sub>2</sub> O <sub>3</sub> -----	.60 -----	.03
SiO <sub>2</sub> -----	15.8 -----	.92
Bases -----	3.4 -----	.20
Total	375.00	21.86



The steam for the radiators is supplied by four 500 H.P. boilers located at a central heating plant and conveyed to the different buildings through 8" and 10" mains under approximately 40# pressure at the plant and at the end of the line 15# pressure.

In the old buildings the one and two pipe gravity systems of heating are in use while the newer buildings are equipped with vacuum systems.

Each buildings is connected to the large mains, the pressure being reduced from 40# to 5# when working under desired conditions. The pressures for this year has varied in the different buildings from 0# to 8#. In the vacuum system the maximum vacuum maintained is 10", although as in the above case, a variation has occurred from atmospheric pressure to 10" vacuum. Pumps at varied distances are maintained on the return lines to draw the water out, and as would be expected, the buildings near the pumps get the benefit of a better vacuum than those at a greater distance. Specific examples will be given (12) that will show this factor to be a very important one.

The discharged water from the buildings is carried back to the heating plant and there allowed to settle in a hot well to be used for the boilers again. From 1/2 to 3/4 of the original amount of water is used over again under excellent working conditions. The boilers evaporate and furnish to the heating system approximately 237,400 gallons of water daily, which would furnish approximately 2# of ammonia through the system per day, if raw water were continually being used.





## PART III.

Corrosive Action of the University Radiator Water on  
Steam Fittings.

## Introduction.

Corrosion tests on copper and brass were made in the laboratory to determine, if possible, the action of small amounts of ammonia and absorbed carbon dioxide on copper and brass fittings.

Experiments were carried out in 250 cc. and 500 cc. Erlenmeyer flasks. The waters used were the samples from the various radiators that contained an excessive ammonia content. The copper strips for corrosion was obtained from the floats that are used in the radiator steam traps and the brass strips from old discarded fittings. These strips were carefully weighed on a five place assay balance after washing and drying with alcohol and ether. Attempts were made to carry out corrosion experiments at temperatures between  $95^{\circ}$  and  $100^{\circ}$  C, as these temperatures correspond to conditions in actual practice. Much trouble was encountered, the difficulty being that the pressure at this temperature would break the flasks. High pressure flasks of the pear shape type were obtained, and often experiencing similar difficulties, some successful tests were made.

## Experimental.

Table #1 shows corrosion tests of copper in radiator water varying in ammonia content from twenty-four parts per million to one hundred and ninety-two. The results are from tests that were carried out in 250 cc. Erlenmeyer flasks containing radiator water.

It is interesting to note that very rapid corrosion took place during the first three days and at the end of five and eight



days the copper strips did not lose in weight to any extent. An examination of the strips showed considerable tarnishing on one side which was probably a film of copper oxide. We would expect the loss in weight of the copper to vary with the increase in ammonia content of the water. This was not the case in many of the tests as, for example, copper strip #7 which shows a loss of 0.134 mg. in weight per square centimeter of water that contains 120 P.P.M of ammonia, whereas strip #1 shows a loss of .0835 mg. per square centimeter of water that contains 24 P.P.M. of ammonia. These exceptional cases may be due to the varying impurities in the copper, although both strips were taken from the same disc. In actual practice these discs were found to be corroded very differently. In some cases corrosion took place on the bottoms of the discs, whereas in other cases the top portions would be attacked.

The corrosion of copper from two types of floats, the discs and balls are shown in the table. There is a very marked difference in the rate of corrosion of the copper obtained from the disc and the ball. In every case the strips from the round balls show a much greater loss. Table II. gives the results obtained from the corrosion of copper strips in synthetic ammonia water. The synthetic ammonia water was made up to correspond as nearly as possible to the ammonia content of the various waters obtained from the radiators in order to obtain comparative results. The copper strips used in these tests were from the same material as is used in experiments of Table #1. These corrosion tests show that the rate of corrosion was much faster than in the corresponding radiator water. As this synthetic water was made up by adding ammonia to distilled water, we can conclude that the mineral or organic content of the radiator







TABLE I.

## Corrosion of Copper in Radiator Water

Test No.	P.P.M. NH <sub>3</sub>	Loss in wt. in 3 days	Loss in wt. in 5 days	Loss in wt. in 8 days	Remarks.
(1) Copper from disc.	24	0.0835	0.0835	0.0835	No signs of tarnishing; water very slightly blue
(2) Copper from round ball	42	0.02550	0.2560	0.0255	Slightly tar- nished; water slightly blue
(3) Copper from round ball	72	0.4460	0.5230	0.5280	Tarnished; water blue
(4) Copper from round ball	96	0.843	1.160	1.180	Tarnished; water blue
(5) Copper from disc.	108	1.750	1.761	1.765	Copper black water very blue.
(6) Copper from round ball	108	0.3619	0.374	0.374	Tarnished on one side
(7) Copper from disc.	120	0.1340	0.1340	0.1340	Tarnished very slightly
(8) Copper from round ball	192	0.869	0.972	0.978	Tarnished on one side.



TABLE II.

## Corrosion of Copper Strips in Synthetic Ammonia Water.

Loss in weight of Mg. per sq. cm.					
Test No.	P.P.M NH <sub>3</sub>	Loss in wt. in 1 day	Loss in wt in 17 days	Loss in wt. in 20 days	Remarks.
Copper strip from ball	220	0.702	1.160	1.162	Water very blue Copper strips black
Copper strip from ball	220	0.625	0.980	0.990	Copper black on 1 side; water very blue
Copper from round ball	120	0.146	0.4170	0.4170	No apparent oxidation
Copper from flat disc	120	0.7350	1.650	1.670	Slightly oxidized one one side
Copper from round ball	82	0.286	0.286	0.286	Very slightly tarnished
Copper from round ball	82	0.245	0.360	0.360	No signs of tarnish
Copper strip f flat disc	60	0.04350	0.1090	0.109	No signs of tarnish
Copper from flat disc	60	0.210	0.210	0.210	No signs of tarnish
Copper strip from flat disc	48	0.320	0.344	0.346	
Copper from flat disc	48	0.320	0.344	0.347	Duplicate runs
Copper from flat disc	48	0.0865	0.280	0.280	Duplicate runs Metal taken from different portions of same disc.

Corrosion of Brass

	Size	Water	Days	Loss
1. Brass	2.50 x 1.20 cm	200 P.P.M	10	.860
2. Brass	2.50 x 1.20 "	100	10	.200
3. Brass	2.50 x 1.20 "	100	10	.250
4. Brass	2.50 x 1.20 "	20	10	.060
5. Brass	2.50 x 1.20 "	10	10	





water has a retarding action rather than an accelerating one on the rate of corrosion due to ammonia in very dilute solutions. On examination the copper strips in the synthetic ammonia water showed no signs of tarnishing. Evidently, it seems that the mineral or organic matter in the water is responsible for the protective film that forms on the copper strips. The corrosion of copper strips in the synthetic ammonia water varies considerably under the same conditions as has previously been shown to take place in the radiator water. Not knowing the exact composition of the copper in either the discs or balls, it was thought that corrosion experiments in which pure copper in synthetic ammonia water would probably throw some light on the irregularity of corrosion as the results in Table I and II show. The results of these tests are shown in Table III. These tests show that the rate of corrosion of pure copper is very fast for the first twenty-four hours and gradually becomes less until corrosion ceases. At the end of three days a protective film began to form on strips #2,3,4 and 5, whereas strip #6 which was in water containing 540 P.P.M. of ammonia only showed a very faint tarnishing effect at the end of six days.

The small loss of strip #3 in comparison with #5 and #5 can not be accounted for as the three were under similar conditions. Results in Table IV show the actual weights of the copper and brass strips that were used in the tests. It is interesting to note that in every case with the exceptions of #7 and #8 a gain in weight was obtained instead of a decrease. Comparing these results with those of Tables II, we would expect that a decrease in weight of the copper strips occurred during the first few hours, and afterwards a protective covering was formed. All of the copper strips when



TABLE III

Corrosion of Pure Copper Strips in Synthetic Ammonia  
Water, Temperature 20° C.

Loss in weight in Mg. per sq. cm.

P.P.M. NH <sub>3</sub> in water	Loss in one day	Loss in two days	Loss in three days	Loss in five days	Loss in six days	Remarks
(1) 2.40	.0114	.0114	.0114	.0114	.0147	Very little tarnish
(2) 1.20	0.294	0.265	0.294	0.294	.294	Tarnished in spots
(3) 240	0.180	0.216	0.294	.279	.294	Tarnished in spots
(4) 240	0.680	1.010	1.110	0.706	1.000	Very tarnished
(5) 240	0.625	0.770	0.975	0.860	0.890	Very dark
(6) 240	0.920	1.180	1.370	1.480	1.620	Very little tarnished

TABLE IV.

Corrosion of Copper & Brass in Radiator Water 95° C.

Pure	Size	Water	Wt. Mar. 20	Wt. Mar. 24	Gain	Loss
(1) Copper strip	12x 1.5 cm	120 PPM	6.6320	6.63380	.0018	
(2) Copper strip	12 x 1.5 cm	120	6.7825	6.7866	.0041	
(3) Copper strip	12 x 1.5	160	6.8215	6.8262	.0053	
(4) Copper strip	12 x 1.5	200	6.7420	6.7476	.0056	
(5) Copper strip	2.50 x 1.25	50	1.29750	1.29690	.00060	
(6) Copper strip	2.50 x 1.25	40	1.12310	1.12200	.001	
(7) Copper strip	2.50 x 1.25	200	1.67210	1.67200		.0001
(8) Copper strip	2.50 x 1.25	100	1.35380	1.35000		.0038







Table IV (Continued)

	<u>Size</u>	<u>Water</u>	<u>Wt.</u> <u>Mar.20</u>	<u>Wt.</u> <u>Mar.28</u>	<u>Gain</u>	<u>Loss</u>
(1) Brass	2.50 x1.20	100	3.4169	3.4160		.0009
(2) Brass	1.25 x1.00	100	0.9060	.90550		.0005
(3) Brass	1.25 x1.00	50	0.8270	.8272	.0002	
(4) Brass	1.25 x1.00	50	Lost			

TABLE V.

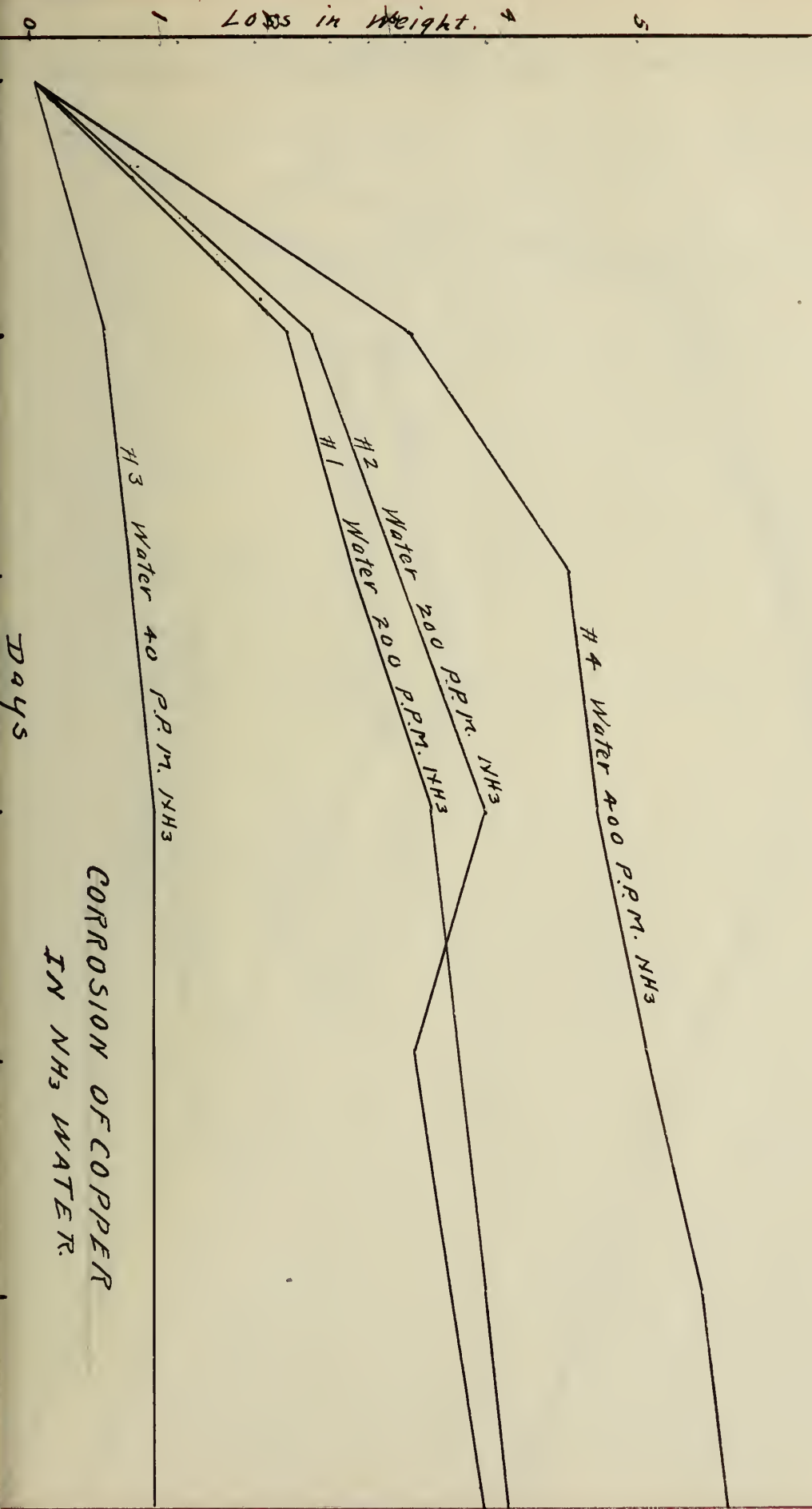
Corrosion of Copper &amp; Brass in Radiator Water at Room

Temperature to Compare with Tests at 95° C.

	<u>Size</u>	<u>Water</u>	<u>Wt</u> <u>Mar.20</u>	<u>Wt.</u> <u>Mar.28</u>	<u>Gain</u>	<u>loss</u>
(1)Same as #1 in Table IV.	12 x1.5	120	6.82160	6.82035		.00125
(2)Same as #3 in Table IV	12 x1.5	160	6.64020	6.63635		.00385
(1)Same as #1 in Table IV	2.50 x1.20	<u>Brass</u> 100	5.8843	5.8830		.0013
(2)Same as #2 in Table IV	1.25 x1.00	100	5.3898	5.3893		.0005
(3)Same as #3 in Table IV	1.25 x 1.20	50	1.3589	1.3586		.0003



#1.

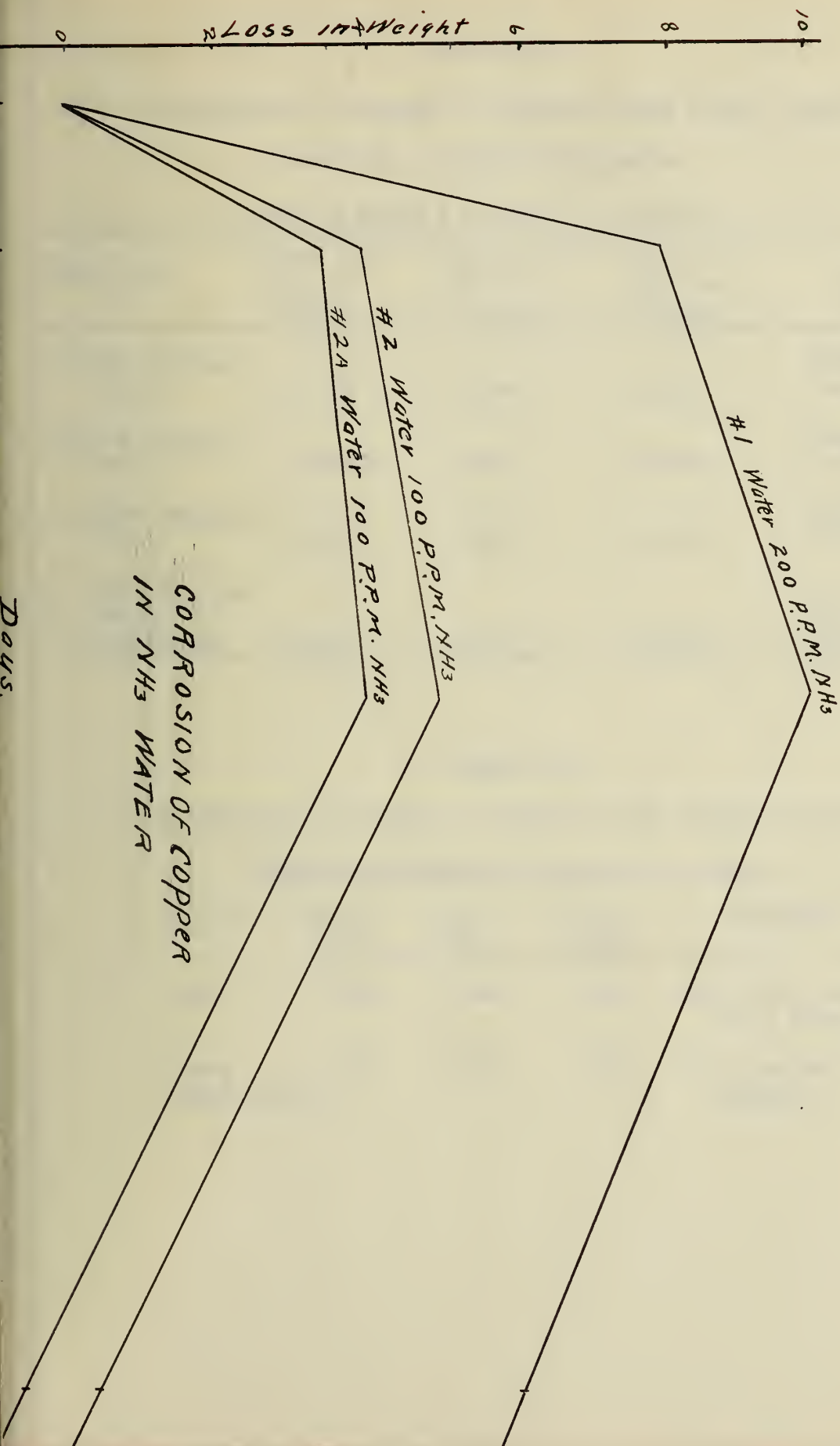


CORROSION OF COPPER  
IN  $\text{NH}_3$  WATER





#2.



CORROSION OF COPPER  
IN  $\text{NH}_3$  WATER



TABLE VI.

Corrosion of Copper in Ammonia Free Water Saturated  
with CO<sub>2</sub> at 20° Centigrade.

Loss in Weight in Mg. per sq. cm.

Material	Loss in wt. 1 day	Loss in wt. in 3 days	Loss in wt. in 5 days	Remarks
1. Pure Copper Foil	0.100	0.166	0.166	Copper foil tarnished black
2. Pure Copper Foil	0.0750	0.166	0.250	Copper foil tarnished black
3. Pure Copper Foil	0.092	0.170	0.170	Copper foil tarnished black
4. Pure Copper Foil Duplicate	0.084	0.167	0.200	Copper foil tarnished black

TABLE VII.

Corrosion of Brass in Ammonia Free Water and CO<sub>2</sub> at 20°C

Loss in Weight in Mg. per sq. cm.

Sample	Days 10	Days 20	Days 30	Remarks
Brass	.100	.190	.270	Slightly blue on 1 side.
Brass (Duplicate)	.100	.173	.251	No apparent change.





examined after the fourth day were extremely black whereas the brass did not show any signs of corrosion

For comparison, corrosion tests on copper and brass were made at room temperature, using the same water as was used in experiments at 95°C. These results (Table V ) show that a decrease in weight took place with both the copper and brass strips. As it has been shown that large volumes of gas containing high percentages of carbon dioxide pass through the steam traps that contain copper floats it was thought essential to try to determine, if possible the corrosive effects this gas has on copper and brass . In Table A are the results obtained for pure copper. Corrosion tests on strips #1,2,3,and 4 were carried out under similar conditions and as shown from results fairly uniform results were obtained. The corrosive action of carbon dioxide resembles the corrosive action of ammonia in every respect. In the case with brass no appreciable corrosive effect was found to take place during the first five days. Tests for ten, twenty, and thirty days were made as shown in Table



## SUMMARY.

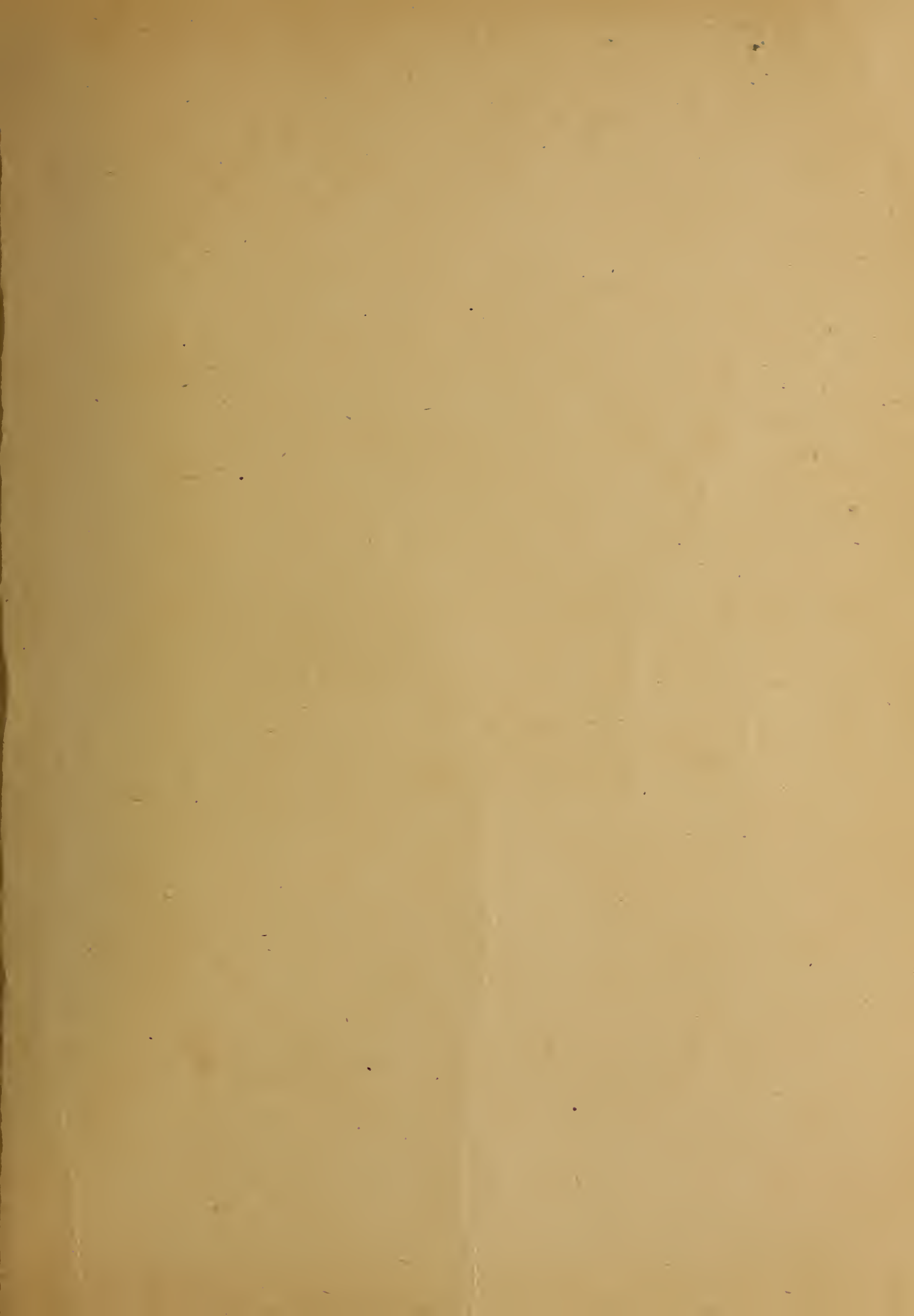
1. Gases were found to collect in almost all steam radiators
2. The quantity and composition of the gases vary within wide limits; the analysis shows large amounts of carbon dioxide and oxygen present.
3. The carbon dioxide absorbed in the water has a decisive corrosive action on copper and brass.
4. The radiator waters contain varying amounts of ammonia.
5. Copper in the presence of very small amounts of ammonia dissolved in water corrodes rapidly.
6. Protective coating is formed on copper where the ammonia content of the water is low.
7. Brass does not corrode as rapidly as copper in water containing small amounts of ammonia.

## References.

1. Journal of the Institute of Metals. No.1 Vol. XV 1916
2. The Corrosion of Metals, Ferrous and Non-Ferrous  
Reprint, Transactions Faraday Society. Vol. XI 1916
- 3&4-Dennis Gas Analysis, Text.
5. Page 21, This Thesis.
7. Dr. H. B. Friend, Corrosion of Iron
8. Dr. W. R. Whitney, American Chemical Society, Vol.25, 1903
- 9&10-Domestic Engineering, Vol. 78 #6, Feb. 19, 1917.
- 11.Dunston, J. American Chemical Society, 22-1548
- 12.Metallic Structures, Corrosion. J. Newman.







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